

## Studies on high temperature deformation behaviour of 3Y-TZP ceramics

D D UPADHYAYA, S K ROY, G K DEY and S BANERJEE  
Metallurgy Division, Bhabha Atomic Research Centre, Bombay 400 085, India

**Abstract.** The present work reports the results on the deformation behaviour of  $ZrO_2$ -3 mol%  $Y_2O_3$  (3Y-TZP) ceramics which were prepared by pressureless sintering at 1400°C. Dense, cylindrical samples were subjected to uniaxial compression tests under a constant stress of 15 MPa in the temperature range of 1200-1400°C. The ceramics exhibit considerable ductility, attaining over 60% true strain without any edge cracking. Microstructural changes due to interaction of grain boundary viscous phase with the ultrafine and equiaxed grains were analyzed by transmission electron microscopy. Results show the grain boundary sliding accompanied by a diffusion accommodation process as the predominant deformation mechanism in these ceramics.

**Keywords.** Yttria stabilized zirconia; superplasticity; microstructure; TEM.

### 1. Introduction

$Y_2O_3$  stabilized tetragonal  $ZrO_2$  polycrystals (Y-TZP) form one important class of transformation toughened ceramics. These  $ZrO_2$  based alloys are promising structural materials for various high performance applications because of their excellent mechanical properties such as strength and toughness. It has also been observed that these ceramics fulfil many of the microstructural prerequisites that have been established for superplasticity in metals and alloys. Subjecting ceramics to deformation forming is thus an important recent advancement in fabrication technology (Panda *et al* 1988; Chen and Xue 1990). Dense Y-TZP ceramics obtained on sintering at moderate temperatures (~ 1400°C) exhibit a homogeneous single phase (tetragonal- $ZrO_2$ ), microstructure consisting of ultrafine (<1.0  $\mu m$ ) and equiaxed grains. The impurities introduced during processing often contribute to the grain boundary liquid phase by the formation of low temperature eutectic melts (Lang *et al* 1986). Extensive studies have been carried out in tailoring a microstructure which is stable against coarsening during deformation at elevated temperatures. A suitable modification of grain boundary chemistry by incorporating some system specific dopants (MnO, CoO) and by providing a composite configuration with other oxides (e.g.  $Al_2O_3$ ) is usually followed in these systems (Kimura *et al* 1988; Wakai 1989; French *et al* 1990; Upadhyaya *et al* 1993a, b).

The mechanism of superplasticity in ceramics is not fully understood. It is generally explained in terms of models based on the grain boundary sliding or diffusional flow mechanisms (Wang and Raj 1984; Wakai *et al* 1989). The constitutive equation for deformation in polycrystalline samples at elevated temperature has the form:

$$\dot{\epsilon} = A (\sigma^n / d^p) \exp (-Q/RT), \quad (1)$$

where  $A$  is the deformation mechanism dependent function,  $d$  the mean grain size,  $p$  the grain size exponent and  $n$  the stress exponent (reciprocal of strain rate sensitivity). The other symbols in above equation have the usual significance.

For Y-TZP ceramics, a large discrepancy appears in the value of  $n$  reported by different authors (from 1.1 to 3.5) (Wakai 1989). The difference in behaviour and a predominantly non-Newtonian flow ( $n > 1$ ) mechanism is likely to be dependent on the concentration and nature of the grain boundary glassy phase. Present work tries to analyze the interaction mechanism of the two microstructural parameters, viz. the rigid grains and soft boundary phase (glassy) in 3Y-TZP ceramics at high temperatures, under compressive loading conditions using TEM as a tool.

## 2. Experimental

The wet chemistry, co-precipitation route was employed to prepare fine powder of  $ZrO_2$ -3 mol%  $Y_2O_3$ . The starting material was 3N purity salts of  $ZrOCl_2 \cdot 8H_2O$  and  $Y(NO_3)_3 \cdot 5H_2O$ . Mixed solutions (0.5 M) were added drop wise into a vigorously stirred liquor ammonia bath which produced a white, gelatinous substance precipitated. These hydroxide gels were filtered, washed, dehydrated with ethanol and dried in air oven at 110°C. The dried mass was pulverized, calcined at 600°C for 3 h and ball milled for 8 h using Y-TZP grinding medium.

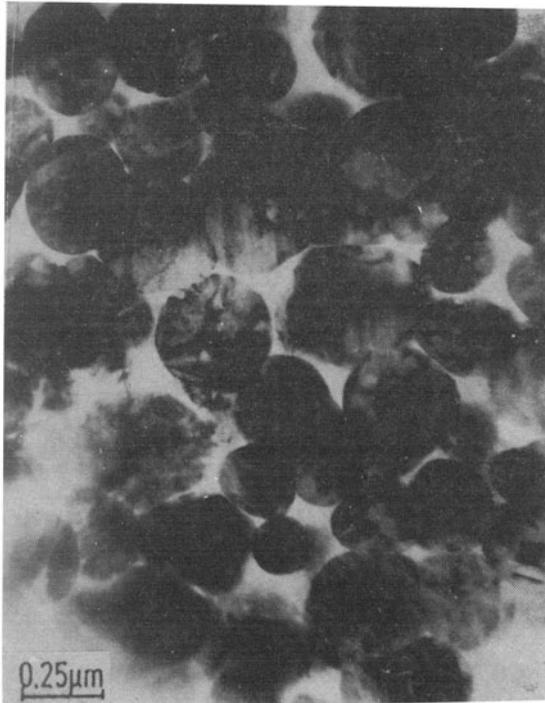
Cold compacted (84 MPa) samples on sintering at 1400°C for 2 h attained nearly full (98% TD) densification. Test samples (10 mm height  $\times$  10 mm diameter) were prepared with their parallel faces fine polished and coated with BN powder. The uniaxial compression experiments were carried out between 1200 and 1400°C in vacuum ( $10^{-3}$  Pa) at a constant load of 15 MPa. Tests were terminated at a true strain of about -0.6 in order to avoid nonuniform stresses and friction conditions. For microstructural investigations the deformed samples were diamond sawed to about 150  $\mu$ m sections. The 3-mm diameter discs were subsequently prepared by ultrasonic cutter and further mechanically thinned using disc grinder followed by dimple grinding using diamond paste. The final thinning to electron transparency was carried out in an argon ion mill operating at 4 kV. Carbon was deposited on the foils to prevent static charge accumulation during observation. A JEOL 2000 FX microscope was used for studying the microstructure.

## 3. Results and discussion

### 3.1 Undeformed 3Y-TZP ceramics

Microstructural features of the reference material are as shown by the typical micrograph in figure 1. It essentially shows a very fine grain structure ( $\sim$  250 nm) having a narrow size distribution. The as-sintered samples showed a dense structure, such that almost no porosity is found in both inter and transgranular regions. The rounded shape of the grains is characteristic of the milled Y-TZP powders which have undergone densification by liquid phase sintering mode (Lang *et al* 1986; Lin *et al* 1990). The amorphous phase traps impurities and mainly segregates at the grain trijunction and also forming an apparently continuous intergranular thin film.

Presence of glassy phase is beneficial in relieving the residual stresses developed



**Figure 1.** Transmission electron micrograph of undeformed 3Y-TZP showing the rounded grains and glassy grain boundary phase.

during cooling due to anisotropic thermal contraction of  $t$ -ZrO<sub>2</sub> grains (Lin *et al* 1990). In the present material, the grains were thus free from tweed like structure due to strain field contrast found in high purity Y-TZP ceramics having straight boundaries with sharp apexes (Amana *et al* 1992). The grains rather exhibited a distribution of three twin related variants of  $t$ -ZrO<sub>2</sub>. The frequency of occurrence of twins was very large with most of the twins revealing the presence of more than one variant in each grain with the different variants sometimes lying in a triangular arrangement.

Another significant observation was with respect to the occasional presence (in about 5% of the specimen area scanned) of the large ( $> 1\mu\text{m}$ ) grains surrounded by an ensemble of significantly smaller size grains (figure 2). This anomalous growth of solute rich  $c$ -ZrO<sub>2</sub> grains is generally observed in Y-TZP on high temperature annealing (1500°C). Development of such microduplex structure due to equilibrium partitioning of yttria was found to be very effective in maintaining the fine grain size of Y-TZP ceramics (Lang *et al* 1985; Lang 1986). The large grains of the  $c$ -ZrO<sub>2</sub> were irregularly shaped unlike the smaller grains of  $t$ -ZrO<sub>2</sub> which were mostly spherical. Twin like features could be seen in some of the  $c$ -ZrO<sub>2</sub> grains.

### 3.2 Microstructural evolution after deformation

Dense 3Y-TZP samples in the shape of right cylinders were compression-tested

uniaxially at 1200–1400°C which is the thermodynamic stability range of tetragonal phase of  $\text{ZrO}_2$ . The absence of transformation toughening in conjunction with the favourable microstructural parameters viz. ultrafine grain size and residual grain boundary viscous phase imparts appreciable plastic deformation before failure. The change in microstructure is as shown in figure 3(a–c) for the sample strained to 60% at 1400°C. It is observed that some amount of coarsening of grains takes place without affecting their isometric shape. The glassy phase is relocated (squeezed) in the form of thin intergranular film. It was possible to see grain boundary trijunctions having very little or no amorphous phase in between.

About the high temperature plastic deformation of bulk  $\text{ZrO}_2$  alloy single crystals, considerable work has been done over the years. It is mostly the work of Heuer and coworkers (Dominguez-Rodriguez *et al* 1986; Cheong *et al* 1989, 1991; Fries *et al* 1989; Heuer *et al* 1989) which establishes that in Y-CSZ the deformation behaviour is very sensitive to crystal orientation together with other parameters, e.g. solute concentration, temperature and strain rate. Significant solid solution strengthening is observed over the range of compositions studied (9.4–21 mol%  $\text{Y}_2\text{O}_3$ ). The yield and flow stress increase with increasing  $\text{Y}_2\text{O}_3$  content. Similarly,

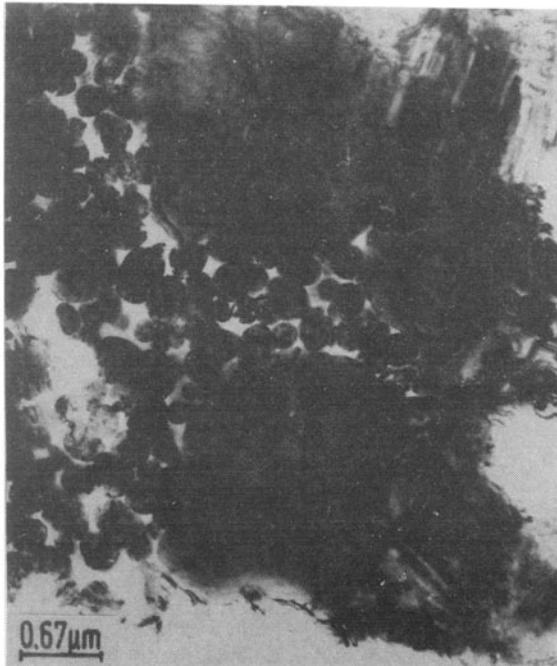
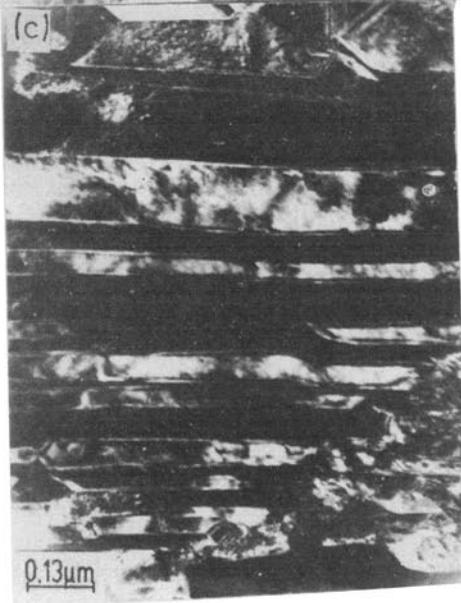
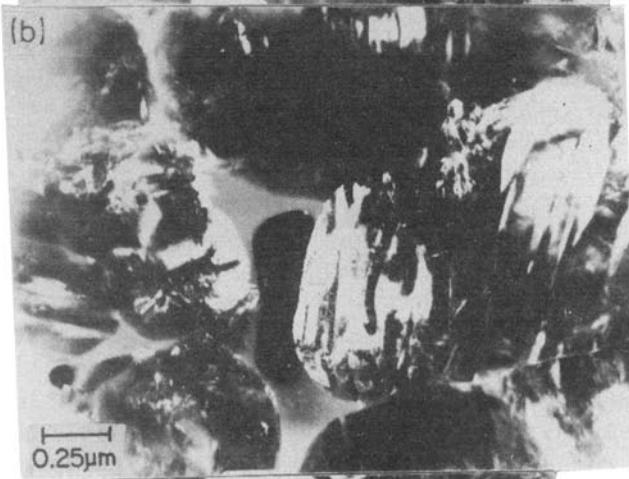
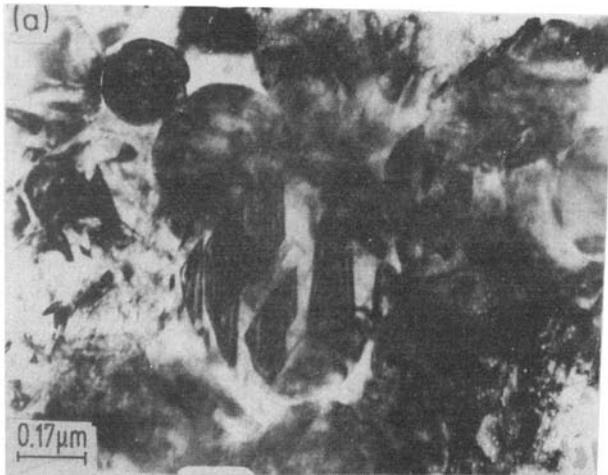


Figure 2. Bright field micrograph showing an occasional bimodal grain size distribution containing coarse  $t$ - $\text{ZrO}_2$  grain surrounded by a much finer  $t$ - $\text{ZrO}_2$  grain cluster.

Figure 3. Microstructural changes after plastic deformation of 3Y-TZP ( $\epsilon = 60\%$ ,  $T = 1400^\circ\text{C}$ ,  $\sigma = 15\text{ MPa}$ ). a. Grains are coarsened but the isometric shape is retained, b. considerable squeezing of the grain boundary liquid into the residual pores and c. stress induced reorientation of ferroelastic domains in  $t$ - $\text{ZrO}_2$ . Two sets of twin variants grow at the expense of third set to facilitate the stress accommodation.



in two-phase Y-PSZ single crystals the phenomenon of precipitation hardening is encountered. In these experiments the stresses employed are generally large ( $> 200$  MPa) and alloy crystals exhibit predominantly a shear band deformation mode accompanied by excessive dislocation activity. Lankford *et al* (1988) supplemented these results by introducing the contributions from transformation plasticity and ferroelastic domain switching.

In the case of polycrystalline  $ZrO_2$  based ceramics the situation is very complex due to grain boundary lubrication by an ubiquitous amorphous phase, for sliding mode to dominate. This permits only a phenomenological explanation by attributing it as the constituent responsible for the viscous-like flow during compression. Maintaining equiaxed grain shape even after extensive deformation is an important aspect which generally suggests a grain intercalation mechanism operating as those visualized in superplastic deformation conditions. An elongation of the grains in the direction perpendicular to the loading axis is predicted if diffusional creep prevails which is contrary to present observations. TEM also revealed that grains were nearly free of dislocations indicating a somewhat minor contribution of dislocation motion in the creep of Y-TZP, in the temperature and stress regimes employed in this work. Though the extent of deformation of the *t*- $ZrO_2$  grains was extremely small, the boundaries between the *t*- $ZrO_2$  and *c*- $ZrO_2$  grains showed considerable amount of waviness in some regions.

The grain boundary amorphous phase has a dual role in influencing the deformation behaviour of Y-TZP. It invariably leads to a strain enhanced dynamic grain growth because of high homologous temperature employed ( $\sim 0.5 T_m$ ). This suggests that grain boundary sliding is accommodated by interface-reaction controlled diffusional creep in the presence of glassy aluminosilicate phase. The model of Pharr and Ashby (1983) describes the liquid enhanced creep on the basis of repetitive cycles of plasticity and dissolution. The macroscopic yielding of 3Y-TZP thus can be rationalized in terms of micrograin superplasticity which is due to the superposition of various mechanisms viz. grain boundary sliding, grain rotation, diffusional accommodation and viscous flow. In addition to this the possible role of important subgrain features of *t*- $ZrO_2$ , i.e. the ferroelastic twin rotation also needs to be evaluated. The domain switching is an intrinsic, thermally activated process involving migration of the interfaces separating the domains. This migration process generates a shear distortion in the fluorite lattice.

TEM is a useful technique for analyzing the change in twinning mode after deformation. Unlike the *t*- $ZrO_2$  grains of the undeformed control sample the grains of deformed specimens showed generally a single twin variant (figure 3c). This fact could be ascertained from the bright and dark field micrographs and corresponding selected area diffraction patterns. Presence of single twin variant was indicative of the occurrence of domain switching. This twin reversal is the unique stress accommodation parameter for 3Y-TZP ceramics and can contribute significantly towards deformation (Lankford *et al* 1988).

The foregoing discussions have pointed to the role of multiple parameters involved in the deformation processing of 3Y-TZP ceramics. From the mechanistic standpoint it can be understood to be completed essentially in three steps. In the initial stage, a lubricated flow begins due to liquid film migration and partial dewetting of the grain boundaries. The flow is sustained in the intermediate stage by solution-precipitation creep. A redistribution of liquid into the residual pores and other

lower energy sites, softens the stress concentration at the grain interfaces. In the final stage the solid–solid contacts are established between the grains and the above mentioned twin reversal process is activated. The different values of strain rate sensitivity exponent measured by different authors for their materials can be attributed to the difference in critical balance obtained between various stress relieving processes.

#### 4. Summary

The present work deals with the superplastic deformation of 3Y-TZP ceramics during compressive creep testing up to true strain near 60% and the resultant microstructural development of the material. TEM results suggest a three-step process sequence basically comprising the redistribution of the grain boundary amorphous phase, the concurrent grain growth due to deformation enhanced diffusion and a stress accommodation due to subgrain ferroelastic domain switching of  $t$ -ZrO<sub>2</sub>. The grain boundary amorphous phase plays a dominant role in controlling the flow properties of 3Y-TZP. The difference in its chemistry thus explains the discrepancy in the reported value of the deformation parameters.

#### Acknowledgements

The authors thank Dr R Bhat and Mr R K Fotedar for their assistance in powder synthesis and compression testing.

#### References

- Amana B, Duclos R and Crompon C 1992 *Ceram. Int.* **18** 1285  
Chen I W and Xue L A 1990 *J. Am. Ceram. Soc.* **73** 2585  
Cheong D-S, Dominguez-Rodriguez A and Heuer A H 1989 *Philos. Mag.* **60** 123  
Cheong D-S, Dominguez-Rodriguez A and Heuer A H 1991 *Philos. Mag.* **63** 377  
Dominguez-Rodriguez A, Lanteri V and Heuer A H 1986 *J. Am. Ceram. Soc.* **69** 285  
French J D, Harmer M P, Chan H M and Miller G A 1990 *J. Am. Ceram. Soc.* **73** 2508  
Fries E, Guiberteau F, Dominguez-Rodriguez A, Cheong D S and Heuer A H 1989 *Philos. Mag.* **60** 107  
Heuer A H, Lanteri V and Dominguez-Rodriguez A 1989 *Acta Metall.* **37** 559  
Kimura N, Okamura H and Morishita J 1988 in *Advances in Ceramics; science and technology of zirconia* (eds) S Somya, N Yamamoto and H Yanagida (Ohio: Amer. Ceram. Soc.) Vol. 24, p. 183  
Lang F F 1986 *J. Am. Ceram. Soc.* **69** 240  
Lang F F, Marshall D B and Porter J 1985 in *Ultrastructure processing of advanced ceramics* (eds) J D Mackenzie and D R Ulrich (New York: Wiley) p. 519  
Lang F F, Schubert H, Clausen N and Ruhle M 1986 *J. Am. Ceram. Soc.* **69** 768  
Lankford J, Page R A and Rabenberg L 1988 *J. Mater. Sci.* **23** 4144  
Lin Y J, Angelini P and Mecartney M L 1990 *J. Am. Ceram. Soc.* **73** 2128  
Panda P C, Wang J and Raj R 1988 *J. Am. Ceram. Soc.* **71** C-507  
Pharr G M and Ashby M F 1983 *Acta Metall.* **31** 129  
Upadhyaya D D, Dalvi P Y and Dey G K 1993a *J. Mater. Sci.* **28** 6103  
Upadhyaya D D, Kuty T R G and Ganguly C 1993b in *Science and technology of zirconia-V* (eds) S P S Badwal, M J Bannister and R H J Hannink (Basel: Technomic Pub.) p. 310  
Wakai F 1989 *Br. Ceram. Trans. J.* **88** 205  
Wakai F, Kodama Y and Nagano T 1989 *Jap. J. Appl. Phys.* **57**  
Wang J G and Raj R 1984 *J. Am. Ceram. Soc.* **67** 399